Pd complex provides the best comparison with that for Fe(100)-H since the enthalpy change of insertion for the Pd complex (-3 kcal/mol) most closely approximates that for Fe(100)-H (-7 kcal/mol). From this viewpoint the activation barrier in complexes may be quite close to the 6 kcal/mol barrier on the Fe(100)-H surface. This indicates that the intrinsic barrier height (i.e. the kinetic barrier if the reaction is thermoneutral) for these reactions on surfaces and in complexes may be quite similar when energies of structural rearrangement are removed from the activation barrier in the complexes.

5. Conclusions

Ethylene adsorbs molecularly on hydrogen-presaturated Fe(100) and undergoes a migratory insertion reaction to form stable ethyl groups. No ethane is formed and no ethylene decomposes on this surface. The insertion reaction proceeds with a preexponential of $10^{8\pm2}$ s^{-1} and an activation energy of 6 ± 1.5 kcal/mol. Competing with ethyl formation is molecular desorption of ethylene, with an activation barrier of 8 ± 2 kcal/mol and a preexponential of $10^{11\pm2}$ s^{-1}. Ethyl groups undergo β-hydride elimination with rate parameters of 13.2 kcal/mol and $10^{13.4}$ s^{-1} for E and A, respectively. Reversible migratory insertion and β-hydride elimination are responsible for multiple H-D exchange for C_2H_4 on a deuterium-covered surface.

Comparison of our results to those for transition-metal complexes indicates that the activation energies for migratory insertion and β-hydride elimination on Fe(100) correlate well with theoretical values for complexes when energetics of ligand rearrangement in complexes are separated.

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Rate Law and Activation Energy of Isotope Mixing between Chemisorbed CO Molecules on a K-Promoted Ni(111) Surface

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Abstract: Laser induced thermal desorption measurements are used to measure the kinetics of isotope exchange between CO molecules chemisorbed on a potassium-promoted Ni(111) surface: $^{13}C^{16}O + ^{12}C^{18}O \rightleftharpoons ^{13}C^{18}O + ^{12}C^{16}O$. The efficiency of the reaction is maximized for a 1:1 K:CO stoichiometry and a 0.3 adspecies/Ni ratio for both K and CO. Over the temperature range 400-525 K the isotope exchange reaction has an apparent activation energy of only 72 ± 4 kJ/mol. Even for long reaction times and high surface temperature, however, the reaction proceeds to only 50% of the statistical limit. To explain these phenomena, we propose that the reaction proceeds via a $K_2C_2O_2$ etherate intermediate adsorbed on Ni(111). This species may be of importance in the promoter action of potassium on CO chemistry on transition-metal surfaces.

Introduction

Activation of the C-O bond in chemisorbed carbon monoxide is one of the most widely studied problems in surface science, yet the primary steps of CO activation are still not well understood at a fundamental level. Several recent reviews highlight the vast body of data on the efficiency of various metallic combinations as catalytic systems.[1] A particularly interesting model system for the heterogeneous catalytic activation of CO is a single-crystal Ni(111) surface promoted by potassium. Although the CO/K/Ni system has received much attention over the past decade, the mechanism for CO bond activation on this important model system has yet to be determined.[1]

CO is relatively unreactive on a clean Ni(111) surface. It bonds to the surface molecularly as terminal and bridge CO species, depending on coverage, and desorbs when the surface is heated to 430 K. CO-stretching frequencies measured by IRAS (infrared reflection absorption spectroscopy) provide a measure of the CO-surface interaction. At full coverage, terminally bonded CO exhibits a CO frequency of 2058 cm^{-1}; bridge-bonded CO exhibits a frequency of 1914 cm^{-1}.[2] These frequencies may be compared to 2143 cm^{-1} for the gas-phase molecule.[3] The bonding of CO on Ni changes dramatically as potassium is added to the surface. The CO vibrational frequency is strongly dependent on the magnitude of both the CO and K coverage.[4] At high K coverages, the CO vibrational frequency drops to near 1400 cm^{-1}, and the CO desorption temperature increases to 640 K.[4] Evidence from metastable quenching spectroscopy suggests that the CO adsorbed at the site with a ~1400-cm^{-1} frequency is nearly parallel with the surface, but the detailed structure is not known.[5] Several different K-CO complexes on different transition-metal surfaces have been proposed, but no conclusive evidence has been presented to support any particular model for the CO/K/Ni system.[5-8]

Another measure of the extent of interaction of CO with the surface is the occurrence of isotope mixing between adjacent CO molecules (i.e. $^{12}C^{18}O + ^{13}C^{16}O \rightarrow ^{12}C^{16}O + ^{13}C^{18}O$). This reaction is especially interesting because it involves complete cleavage of the original CO bonds to make new ones. Ng et al.[9] have shown that this reaction does not proceed with an observable rate on clean Ni(111) in agreement with earlier studies on Ni(100).[10] It has been shown by Ng et al.[9] and Lee et al.[11] that

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(1) *Physics and Chemistry of Alkali Metal Adsorption*; Bonzel, H. P., Bradshaw, A. M., Ertl, G., Eds.; Elsevier: New York, 1989. Bonzel, H. P. *Surf. Sci. Rpt.* **1987**, *8*, 43. Heskett, D. *Surf. Sci.* **1988**, *199*, 67.

(2) Surnev, L.; Xu, Z.; Yates, J. T., Jr. *Surf. Sci.* **1988**, *201*, 1, 14, and references therein.

(3) Huber, K. P.; Herzberg, G. *Constants for Diatomic Molecules*, Van Nostrand Reinhold: New York, 1979.

(4) Uram, K. J.; Ng, L.; Yates, J. T., Jr. *Surf. Sci.* **1986**, *177*, 253. Uram, K. J.; Ng, L.; Folman, M.; Yates, J. T., Jr. *J. Chem. Phys.* **1986**, *84*, 2891.

(5) Arias, J.; Lee, J.; Dunaway, J.; Martin, R. M.; Metiu, H. *Surf. Sci.* **1985**, *159*, L433.

(6) dePaola, R. A.; Hrbek, J.; Hoffmann, F. M. *J. Chem. Phys.* **1985**, *82*, 2484.

(7) Lackey, D.; Surman, M.; Jacobs, S.; Grider, D.; King, D. A. *Surf. Sci.* **1985**, *152/153*, 513.

(8) Solymosi, F.; Berko, A. *Surf. Sci.* **1988**, *201*, 361.

(9) Ng, L.; Uram, K. J.; Xu, Z.; Jones, P. L.; Yates, J. T., Jr. *J. Chem. Phys.* **1987**, *86*, 6523.

(10) Goodman, D. W.; Yates, J. T., Jr. *J. Catal.* **1983**, *82*, 255.

(11) Lee, J.; Arias, J.; Hanrahan, C. P.; Martin, R. M.; Metiu, H. *J. Chem. Phys.* **1985**, *82*, 485.

isotopic mixing in chemisorbed CO occurs when the coverage of potassium is greater than 0.1 (saturation coverage of potassium is approximately 0.36 K/Ni). Remarkably, although the potassium induces the isotope mixing, no effect due to isotope mixing could be observed by IRAS in the 1400-cm^{-1} band.[9] The extent of isotope mixing has only been observed by thermal desorption. This means that there has been no way to monitor the extent of the potassium-catalyzed isotopic mixing reaction below the desorption temperature. Because isotopic mixing was not observed in CO species by using IRAS, Ng et al.[9] postulated that the activated molecules had been completely dissociated to atoms. Another possibility is that the active CO molecules are exactly parallel to the surface and are thus not IR active, i.e., the 1400-cm^{-1} band is unrelated to the CO species undergoing isotopic exchange. Since it has not been possible to directly observe the isotope mixing products *on the surface*, it has also been impossible to measure the kinetics of the isotopic mixing reaction as a function of surface temperature. The range of kinetic possibilities extends from that of a very fast mixing reaction at low temperatures to a mixing reaction only at the high temperatures that induce molecular CO desorption from the surface in a very short time after reaction.

In a recent communication, we have shown that it is possible to monitor the isotope mixing reaction at surface temperatures below which thermal desorption occurs by using the laser induced thermal desorption (LITD) technique.[12] In this paper we report a detailed description of LITD studies performed to measure the rate law as a function of surface temperature to obtain the activation energy for the mixing between the chemisorbed CO isotopes on the potassium-promoted Ni(111) surface. The mixing of isotopes is found to occur at temperatures as low as 400 K, well below the desorption temperatures of CO isotopes and K. The mixing does not proceed to the statistical limit. This implies limited mobility of the CO molecules between reaction sites. The measured activation energy for the mixing of CO isotopes in the presence of potassium is 72 ± 4 kJ/mol. To explain these phenomena, we propose that the mixing reaction occurs via a $K_2C_2O_2$ cyclic etherate complex.

Experimental Section

The techniques used in the present experiments are temperature programmed desorption (TPD) and laser induced thermal desorption (LITD). The TPD technique was used to calibrate the coverages of both K and CO on the surface and also to measure the extent of isotope mixing. The LITD technique was primarily used to measure the rate of isotope mixing of the chemisorbed CO on the K-promoted Ni(111) surface, by analysis of the rate of exchange of carbon and oxygen isotopes between CO molecules as a function of surface temperature. The LITD technique allows the rate law to be determined under isothermal surface temperature conditions.

All experiments were performed in an ultra-high-vacuum (UHV) chamber with a base pressure below 3×10^{-10} Torr that has been described elsewhere.[13] The nickel crystal used in these experiments was 1.7 cm in diameter, oriented to within 0.5° of the (111) direction and polished with diamond paste to 0.5 μm. The crystal was initially cleaned by sputtering with 1-kV argon ions and then annealing at 1300 K. This procedure was sufficient to reduce the impurity levels of sulfur, carbon, and oxygen so that they were not detectable by Auger spectroscopy. The CO isotopes used in these experiments were purchased from Cambridge Isotopes in 1 L glass bulbs. Since the isotopically labeled CO is not 100% enriched in the desired isotopes, the isotopic composition in the absence of any isotopic mixing must be carefully measured. A nominally prepared 1:1 mixture of the $^{12}C^{18}O$ and $^{13}C^{16}O$ gases was analyzed to contain 8 mol % $^{12}C^{16}O$ and 5 mol % $^{13}C^{18}O$ as measured in our UHV system. The stated purity of the $^{12}C^{18}O$ is 97–98% ^{18}O and 99% ^{12}C; for $^{13}C^{16}O$, the stated composition is 10% ^{18}O and 99% ^{13}C. It is likely that the $^{12}C^{16}O$ isotopic species (8 mol %) partially originates from the walls of the sample line and the UHV system.

Potassium was deposited on the Ni(111) surface at 250 K by using a resistively heated commercial SAES getter source. The pressure increase during the K deposition was less than 1×10^{-10} Torr. Potassium coverages, θ_K = K atom/Ni surface atom, were characterized by thermal desorption and LEED. A coverage of $\theta_K = 0.28$ was chosen for these studies because it results in a narrow temperature range of CO desorption as well as the highest yield of CO isotope mixing. The specific calibration procedure to obtain this coverage was to expose the Ni surface at 250 K to multilayers of potassium and then to anneal to 350 K to obtain a monolayer as confirmed by the hexagonal LEED pattern observed for the potassium monolayer coverage. For this monolayer potassium coverage θ_K was taken to be 0.36 as reported by Uram et al.[4] We were able to consistently reproduce a coverage of $\theta_K = 0.28$ by flashing the surface to 450 K and immediately cooling.

CO was dosed onto the Ni(111) surface by using a collimated array doser.[14] Saturation CO coverage for a clean Ni(111) surface was achieved by exposing the surface (at 90 K) for 180 s with a backing pressure of 1 Torr behind the capillary array doser and was taken to correspond to $\theta_{CO} = 0.57$.[2,4] CO coverages for the potassium predosed surface were calibrated by comparison of the CO TPD area to that of CO desorption from clean Ni(111) at CO saturation. The mixture of $^{12}C^{18}O$ and $^{13}C^{16}O$ was dosed onto the potassium precovered surface at 155 K to a coverage $\theta_{CO} = 0.3$.

LITD was performed by using the 308-nm output of a XeCl excimer laser with line-of-sight mass spectrometric detection of the desorbing species. The laser output was apertured and focused to form an elliptical spot approximately 4 by 1 mm on the surface. The laser pulse energy that entered the chamber was approximately 15 mJ. The LITD technique was used to measure the rate of isotopic mixing. For these experiments, K was first dosed to a coverage of $\theta_K = 0.28$ and CO isotopes to a coverage of $\theta_{CO} = 0.3$ as explained above. Next the surface was heated rapidly (4 K/s) to the desired mixing reaction temperature, between 400 and 525 K. The surface was held at this temperature for a specific time and then allowed to cool back to 350 K. Finally, 18 laser desorption shots were performed (with each shot impinging on a different spot on the surface) and the gas desorbed by each shot was monitored by the differentially pumped QMS. The yield of one of the CO isotopes was measured for each shot. The data were averaged, and the isotope mixing ratio, $R = 2I_{31}/(2I_{31} + I_{30} + I_{29})$, was calculated ($I_N$ represents the average intensity of the CO isotopes of mass number N). This particular ratio was used because it is a measure of the fraction of isotope mixing and minimizes the effect of background $^{12}C^{16}O$ contamination.

Results

We report here results obtained for the thermal desorption of CO on both clean and K-precovered Ni(111) surfaces and LITD measurements of the kinetic data obtained from isothermal isotope mixing in the presence of K on the Ni(111) surface.

Figure 1 shows three thermal desorption curves that help to illustrate the cooperative nature of K and CO bonding to the Ni(111) surface. The lower curve shows the CO thermal desorption from a potassium-free Ni(111) surface. The upper two portions of the figure show K and CO desorption curves for $\theta_K = 0.28$ and $\theta_{CO} = 0.3$, the coverages for which the kinetics studies were performed. The CO thermal desorption maximum occurs at 430 K for the potassium-free Ni(111) surface while the potassium-precovered surface shows a high temperature, 630 K, CO desorption state for all the isotopes in agreement with previous studies.[2,4] When both K and CO are present on the surface, the sharp potassium desorption feature closely correlates with the sharp CO desorption feature although detailed differences in peak shape are observable. It is also clear from this figure that extensive isotope mixing occurred between CO molecules on the potassium-covered surface.

Figure 2 shows the results from the LITD studies of the extent of the isothermal isotope mixing reaction as a function of time at several different surface temperatures. The K and the CO overlayer (again, $\theta_K = 0.28$, $\theta_{CO} = 0.3$) was prepared as explained in the Experimental Section. As seen in Figure 2, for surface temperatures between 400 and 525 K, the extent of isotope mixing increases as a function of the time that the surface spends at that particular temperature. The isotope mixing ratio is seen to gradually rise from a value of 0.09, reflecting the intitial isotopic composition of the adsorbed CO gas, to approximately 0.3. Complete mixing would yield a final value of the mixing ratio of 0.5 for a pure sample of isotopes and 0.47 for our mixture. The

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(12) Sinniah, K.; Sands, W. D.; Hrbek, J.; Yates, J. T., Jr.; Janda, K. C. *Surf. Sci.* **1991**, *243*, L67.

(13) Sinniah, K.; Sherman, M. G.; Lewis, L. B.; Weinberg, W. H.; Yates, J. T., Jr.; Janda, K. C. *J. Chem. Phys*, **1990**, *92*, 5700.

(14) Bozack, M. J.; Muehlhoff, L.; Russell, J. N.; Choyke, W. J.; Yates, J. T., Jr. *J. Vac. Sci. Technol.* **1987**, *A5*, 1.

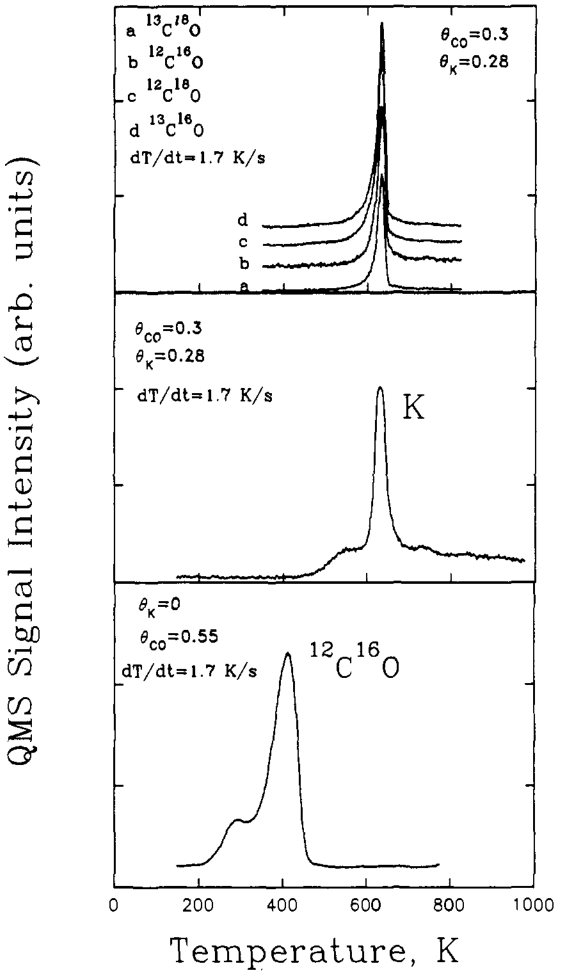

Figure 1. The TPD curves of $^{12}C^{16}O$ on clean Ni(111) (lower figure), potassium (middle figure), and CO isotopes (top figure) resulting when a 1:1 mixture of $^{13}C^{16}O$ and $^{12}C^{18}O$ is coadsorbed with potassium on the Ni(111) surface.

solid line through the data points is a fit to a rate law and was calculated as described below.

Since the desorption spectra common to all CO isotopes have the same shape, we assume that the same rate-determining step governs the desorption of both the reactive and unreactive CO molecules. Further we assume that the isotope mixing rate law has a first-order dependence on the coverage by each isotopic species. Since our initial exposure contained mainly $^{12}C^{18}O$ and $^{13}C^{16}O$ the most important reaction to consider is

$$^{13}C^{16}O + {}^{12}C^{18}O \underset{k}{\overset{k}{\rightleftharpoons}} {}^{13}C^{18}O + {}^{12}C^{16}O \qquad (1)$$

Therefore

$$d[^{13}C^{18}O]/dt = k\{[^{12}C^{18}O]_0 - [^{13}C^{18}O]\}\{[^{13}C^{16}O]_0 - [^{13}C^{18}O]\} - k\{[^{12}C^{16}O]_0 + [^{13}C^{18}O]\}\{[^{13}C^{18}O]_0 + [^{13}C^{18}O]\} \qquad (2)$$

By letting $\theta_0 = [^{12}C^{18}O]_0 + [^{13}C^{16}O]_0 + [^{12}C^{16}O]_0 + [^{13}C^{18}O]_0 = 2a + 2b$ = the initial concentration of all species present, where $a = [^{12}C^{18}O]_0 = [^{13}C^{16}O]_0$ and $b = [^{12}C^{16}O]_0 = [^{13}C^{18}O]_0$, the $^{13}C^{18}O$ coverage as a function of time is given by

$$[^{13}C^{18}O] = (a - b)/2 - \tfrac{1}{2}(a - 3b)\exp(-k\theta_0 t) \qquad (3)$$

The data plotted in Figure 2 correspond to a ratio of the form $2I_{31}/(2I_{31} + I_{30} + I_{29})$ which we will refer to as $R(t)$ as a function of time

$$R(t) = [0.5 - b/2a] - [0.5 - 3b/2a]\exp(-k\theta_0 t) \qquad (4)$$

It is clear from the above equation that if mixing were complete $R(t)$ would go to 0.5 for long times. Figure 2 shows that the limiting value of the isotopic mixing ratio is instead about 0.3. Also, due to isotopic impurities in the initial CO mixture, $R(t{=}0) = 0.09$ rather than zero. Clearly eq 4 cannot be used to fit the data in Figure 2 as it assumes mixing to occur statistically at every site. Hence, we use an equation similar to eq 4 except that the parameters are adjusted to obtain the empirically determined limiting mixing ratio, 0.3, and the initial ratio, 0.09: $R(t) = 0.31 - 0.22\exp(-k\theta_0 t)$. This rate law was fitted to each data set in Figure 2 to obtain values for the rate constant as a function of surface temperature. The error bars shown in the figure are the standard deviation of many measurements. Note that for the 525 K data we used a slightly larger value for the initial isotope ratio in the fit to the data. This is to correct for reaction that occurred during heating and cooling of the surface before the LITD measurement. The corrected initial value was obtained by integrating the rate law over the heating curve. For lower reaction temperatures a similar integration confirmed that negligible reaction occurred during heating and cooling. The data are in good agreement with the assumptions of the analysis at all the measured temperatures.

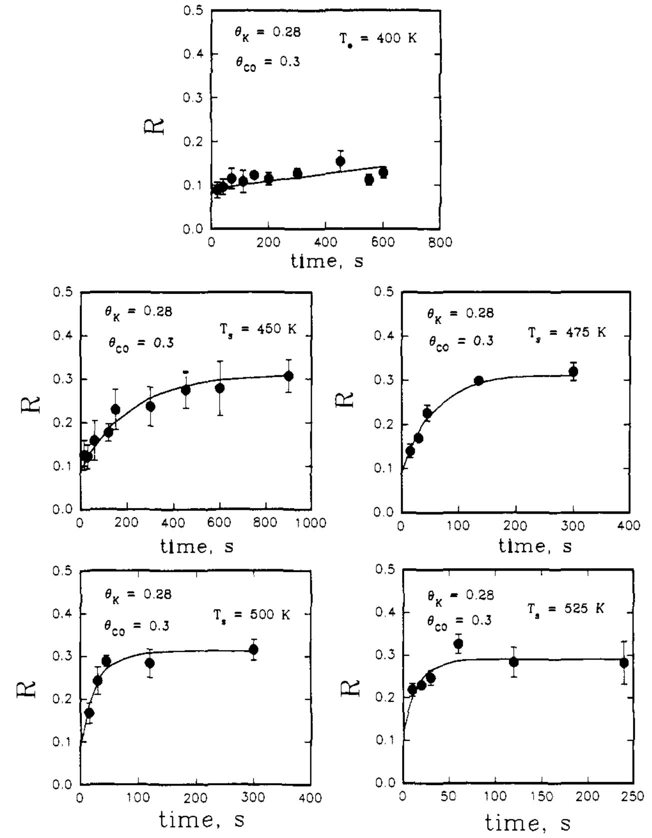

Figure 2. The extent of isotope mixing, R ($R = 2I_{31}/(2I_{31} + I_{30} + I_{29})$), as a function of time for several different temperatures. The error bars for each point on a plot represent the standard deviation of 18 independent shots from LITD experiments. The solid line through the data points is a fit to a second-order rate law as described in the text.

Figure 3 shows an Arrhenius plot of the rate constants as a function of surface temperature obtained from the data in Figure 2. The Arrhenius analysis yields a value for the apparent activation energy of 72 ± 4 kJ/mol and a preexponential factor of $10^{6.5\pm0.5}$ cm^2 s^{-1}.

Discussion

We have shown that the laser induced thermal desorption (LITD) technique can be applied to study the isothermal kinetics of isotope mixing between CO molecules adsorbed on a potassium-promoted Ni(111) surface. Although the CO/K adlayer on the Ni(111) surface has been studied widely over the past decade there is no published report of the observation of isotope mixing at temperatures below the CO desorption temperature. Thus there are no previous measurements for the kinetics of the

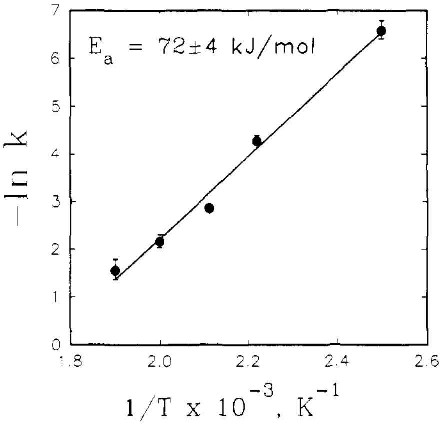

Figure 3. Arrhenius plot for the isotope mixing of CO on potassium-promoted Ni(111). The apparent activation energy for the mixing of isotopes is 72 ± 4 kJ/mol.

reaction. In a preliminary report of this work[12] we showed that the CO isotopes begin to mix around 400 K, well below the CO- and potassium-desorption temperatures. The present study is the first to measure the rate of mixing as a function of temperature. We have measured the rate law for the isotope mixing reaction over the temperature range of 400–525 K and have determined that the activation energy for the reaction is 72 ± 4 kJ/mol. Another very important result of this study is that the extent of isotope mixing is incomplete even for long reaction times. While the extent of mixing depends on the initial potassium and CO coverage,[9] it is independent of surface temperature within our experimental sensitivity.

The interactions of K and CO on the Ni(111) surface are highly synergistic. In temperature-programmed desorption studies, the two species desorb over the same temperature range. For $\theta_K > 0.1$, the CO-desorption range is very narrow at 630 K. This is 200 K higher than the CO-desorption temperature on clean Ni(111). In the absence of CO on the surface, the potassium desorbs over a very broad temperature range as is characteristic of adsorbates that bond strongly to the surface, but repel one another.[11] Clearly, there is extensive charge transfer between the potassium and the Ni surface, and this charge transfer has profound effects on the CO bonding to the surface. Ishi et al.[15] were able to model the thermal desorption barrier using a model in which the CO and potassium bond to the Ni at separate, not mutually exclusive sites, but with a CO–Ni interaction that is a strong function of potassium coverage.

It is tempting to invoke the Blyholder effect[16] to explain the strengthening of the Ni–CO bonding and the decrease in the C–O stretching frequency as a function of increased potassium coverage. This is probably overly simplistic, however, because both the bonding change and the frequency change are much more extensive than would normally fall into the range of the Blyholder effect. Also, the metastable quenching spectra[5] indicate that the CO is not perpendicular to the surface in the limit of the strongest bonding conditions.

The evidence for CO bonds oriented parallel to the surface[5] and the incomplete isotope mixing at long times have suggested a model for the CO/K/Ni interaction that involves the formation of $K_m(CO)_n$ complexes on the surface. Such complexes would explain the incomplete mixing since they would reduce the mobility of CO. They would also explain why CO and potassium desorb together over a very narrow temperature range. We attempted to observe formation of such complexes using the LITD technique but were not able to see any mass signals due to any $K_m(CO)_n^+$ fragment long lived enough to be detected. Since any clusters chemisorbed on the surface may not be stable in the gas phase, this negative result does not argue too strongly against complex formation on the surface. In the future, we will attempt to observe direct laser desorption of anions, which should be a more sensitive probe of the formation of clusters.

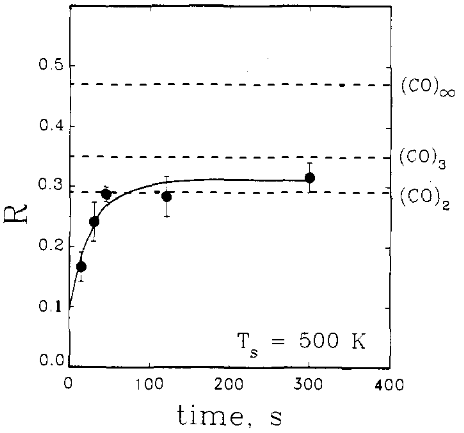

Figure 4. The extent of isotope mixing is plotted as a function of time at 500 K. Assuming our initial isotope composition ($R = 0.09$), the limiting ratio measured experimentally is 0.3. If each active site contains two CO molecules then the expected limiting ratio is 0.29. If each active site contains 3 CO molecules then the limiting mixing ratio would be 0.35. Complete mobility between active sites (for our sample) would result in a value $R = 0.47$. The data are in good agreement with the prediction of two CO molecules per active site.

The limited extent of isotope mixing can be used to infer how many CO molecules are isolated in a reaction site. For instance, if there are two CO molecules per site, and two CO isotopic species are initially adsorbed, then there is an equal probability that the site contains two isotopically identical species or one of each. Clearly, no isotopic mixing will be observed if the two isotopic CO species are identical. If we assume that mixing goes to the statistical limit at the sites with one of each isotopic CO species, then overall 25% of the adsorbed molecules will be converted to mixed species, and the observed isotope ratio, R, will be 0.25. Taking into account our initial isotopic composition, the predicted limiting value of R is 0.29 for two CO molecules per active site. Within experimental error this is equal to the observed limiting ratio of 0.3. The expected isotope mixing ratio goes up as the number of CO molecules per active site increases. For statistical mixing within a site that contains three CO molecules, and for the adsorption of an equimolar ratio of isotopic CO species, the expected limiting ratio is 0.33. For our CO mixture the limiting ratio would be 0.35, for three CO molecules per active site.[17] Thus the data imply that there are two CO molecules per active site, and a complex of formula $K_x(CO)_2$ is the active species. This is illustrated in Figure 4.

It is interesting to note that for the experiments performed in this study, $\theta_K = 0.28$ and $\theta_{CO} = 0.3$: on average, there is one CO per potassium atom. These happen to be the coverage conditions that give the narrowest TPD curve and the maximum overall isotope mixing yield. In particular, for these conditions, very little CO thermally desorbs from the surface below the temperature at which the entire overlayer desorbs. This implies that under these conditions all of the CO are in active sites. Therefore, the most likely active species is $K_2(CO)_2$.

The gas-phase value for the CO bond energy is 1076 kJ/mol. Clearly, the CO bond is not this strong on the potassium-promoted Ni surface. For the lowest frequency species so far observed, the stretching frequency is reduced to ~1400 cm^{-1}. Still, 1400 cm^{-1} is approximately characteristic of a C–O single bond, with an approximate dissociation energy of 400 kJ/mol. The measured value of the apparent activation energy for isotope mixing is only 72 kJ/mol. This implies that the isotopic mixing reaction is a concerted process and supports the model that a specific complex

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(15) Ishi, S.; Asada, H.; Ohno, Y. *Surf. Sci.* **1986**, *171*, L441.

(16) Blyholder, G. *J. Phys. Chem.* **1964**, *68*, 2772.

(17) Calculation of the expected mixing ratio as a function of cluster size is complicated by the gradual contamination of the surface by $^{12}C^{16}O$ from the chamber. For our starting mixture (5% $^{13}C^{18}O$, 8% $^{12}C^{16}O$, 42% $^{12}C^{18}O$, 45% $^{13}C^{16}O$), the expected final mixing ratios are 0.29 for $(CO)_2$ and 0.35 for $(CO)_3$.

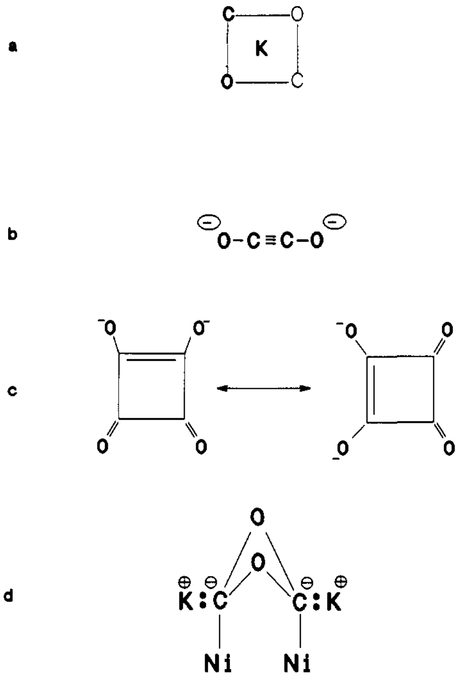

Figure 5. Proposed K–CO complexes: (a) complex formed by dative bonding of CO to a potassium atom as proposed in ref 5; (b, c) anionic complexes observed for CO bonded to potassium-promoted Cu(110) (ref 7); (d) proposed $K_2(CO)_2$ etherate complex based on the stoichiometry obtained from the present experiment.

is involved in the reaction. In fact, the activation energy is so low that it severely limits the type of complex that could serve as the active intermediate.

One suggested type of complex involves dative π electron donation from the CO adsorbate to the potassium atoms as illustrated in Figure 5a. Arias et al.[5] pointed out that such a species could account for the limited extent of isotope mixing. Several investigators[18] have shown that such complexes can be formed between CO molecules and Li atoms in inert matrices. It seems unlikely, however, that dative bonding would be sufficient to lower the activation energy for isotope mixing to 72 kJ/mol.

A second type of complex proposed for CO on potassium-promoted transition-metal surfaces involves $(CO)_n^{2-}$ anions. For $n = 2$, the bonding is $OC{\equiv}CO^{2-}$ (Figure 5b), while for $n = 4$ the anion has a square-planar, aromatic structure illustrated in Figure 5c. Such species have also been observed in rare gas matrices,[18] and their infrared spectra are quite similar to that observed for CO bonding to K-promoted Cu surfaces.[7] Again, however, given the bonding arrangement in such clusters, it is not clear how the C–O bonds could rearrange in such a complex without a substantial activation energy.

On the basis of the stoichiometry of the complex proposed here, $K_2(CO)_2$, and the low activation energy for isotope exchange we propose that a third type of complex intermediate should be considered. Our proposed structure, shown in Figure 5d, is a ring structure incorporating two CO molecules. It involves dative bonding between each carbon atom to a potassium cation, covalent bonding between each carbon and the Ni surface, and an ether-like linkage of the carbon atoms by the two oxygen atoms. Since this structure satisfies the bonding requirements of each atom involved, and since the ionic interaction between the potassium and carbon atoms offsets the negative formal charge on the carbon atoms, it is possible that the structure is formed with a relatively low activation energy. Since the two oxygen atoms are in equivalent positions in this complex, it is clear that CO isotope mixing would be complete upon desorption for etherate complexes formed from different isotopes.

It is not obvious at this time whether the proposed intermediate would be a stable species, formed by a process with a 72-kJ/mol activation barrier, or whether the intermediate is itself the transition state between reactants and products. We had hoped to investigate this issue by sequential dosing experiments. By dosing first with $^{12}C^{18}O$ and then with $^{13}C^{16}O$, and observing the extent of isotope mixing, we hoped to explore at what stage in the reaction the individual molecules are incorporated into an active site. Unfortunately CO incident on the surface can displace CO already adsorbed on a surface at temperatures down to 120 K, and this greatly complicates the analysis of sequential dosing experiments. So far, we have *not* observed any decrease in the extent of mixing by forming complexes of one isotopic species before dosing with the other.

An advantage of a mechanism in which the proposed intermediate is stable is that this would explain the previous failure to observe isotope mixing by IRAS. Formation of the etherate complex would cause an abrupt shift of the C–O stretch out of the frequency range of the spectrometer employed by Ng et al.[9] Consequently, it is clear that further vibrational studies of the region near 1100 cm^{-1}, corresponding to a C–O ether stretching mode, would be very useful to investigate the validity of our proposed complex species.

It is important to consider how the intermediate proposed here can rationalize the large number of previous studies of the behavior of CO on alkali-promoted transition metals. For $\theta_K < 0.28$ on Ni(111) the extent of isotope mixing between CO molecules decreases until $\theta_K \sim 0.1$ at which point the reaction stops altogether. Reduced reactivity at $0.1 < \theta_K < 0.28$ can be explained by the fact that at lower coverage all the active sites may be filled by a fraction of the CO molecules and that there is low mobility between active and inactive sites. There are several feasible explanations why the mixing reaction does not proceed below $\theta_K = 0.1$. For instance, the ionic repulsions between potassium atoms may hinder complex formation. Also, $K_x(CO)_y$ complexes of different stoichiometry and structure may be produced at low coverages. Similarly, the type of complex formed may be very sensitive to the strength of bonding between the CO and the metal substrate. This could help explain the different extent of reactivity of different transition metals. To investigate these issues further, it will be very important to measure how the activation energy for isotope mixing depends on the transition-metal substrate, the alkali promoter, and the coverage of alkali atoms.

Summary

In summary, we have found that for the specific coverage $\theta_K = 0.28$ and $\theta_{CO} = 0.3$ on a Ni(111) surface the isotope mixing reaction proceeds only to 50% of the statistical limit with an empirical activation energy of 72 kJ/mol. This reaction is observed to begin near 400 K, using LITD analysis methods. These observations are consistent with the formation of an etherate complex $K_2(CO)_2$ bound to the Ni surface. The formation of this complex under other conditions of surface coverage remains to be studied. This species may be involved in potassium-promoted catalytic chemistry of carbon monoxide.

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(18) Krishnan, C. N.; Hauge, R. H.; Margrave, J. L. *J. Mol. Struct.* **1987**, *157*, 187. Manceron, L.; Perchard, J. P. In *Physics and Chemistry of Alkali Metal Adsorption*; Bonzel, H. P., Bradshaw, A. M., Ertl, G., Eds.; Elsevier: New York, 1989; pp 403–412.